

1. Introduction

Nowadays all experts involved in conservation of cultural heritage have to deal with the effects of past and even relatively recent restorations, in cases where it has lead to degradation and where application of restoration criteria and methodology still lack deep scientific research. This deficiency is even more accentuated in the case of archaeological sites. Since the 50's and 60's, with the arrival of synthetic polymers and other chemical products used for cleaning, consolidating or protecting cultural heritage, new products have been used indiscriminately, with no previous knowledge of its effects on archaeological remains. This being an experimental discipline undoubtedly entails remarkable advantages, as well as a considerable number of risks, especially when some techniques and products are used or applied with no previous laboratory testing.

For different reasons, other disciplines in the field of conservation science, such as painting or architecture, even restoration of archaeological objects, have demonstrated certain concern on the effects or alterations caused by former treatments. The conservation of archaeological sites, a relatively modern discipline (in systematic and scientific terms), is a complex discipline where too many factors apply and the particularities and individual features of each site preclude the application of universal rules. Research in stone conservation also has a long tradition in identification of pathologies, mechanisms of degradation and development of treatments. However, the effects of some of those treatments in the mid and long-term are still poorly described.

Few studies have been conducted on the effects that conservation interventions have had on original stone material after some years, even decades, and most of them focused on the conservation of historical buildings and on consolidation and hydrophobic or protective treatments [1-10].

Merida is an ancient Roman city that was listed World Heritage Site by UNESCO in 1993 (Figure 1). Excavation began in 1911 and the first restorations were performed in the early 20's with the anastylosis project on the theater (Figure 2). For this case study we count with an evolution of criteria, techniques and products, since the early 20's until the present day, thus showing a wide range of analysis cases.



This research is initially focused in two archaeological areas, House of Mitreo (1) and Roman Theater (2) (Fig.1).

2. General goals

Taking into account the above mentioned considerations, the project carried out within the framework of CEI Campus Moncloa has the following specific goals:

- Review of restoration interventions, and more specifically superficial treatments, applied to the archaeological heritage throughout the twentieth century and during the early years of this century.
- Physic-chemical analysis to determine the effects of the interaction of restoration products on the original substrate, and evaluation of their effectiveness.
- Validation, or dismissal, of treatments and the establishment of standard operating protocols to develop more respectful intervention methods with the particular conditions of archaeological sites.
- Encourage monitoring of interventions throughout the use of portable field devices, as well as fostering the use of non destructive techniques of analysis.
- Analysis of compatibility between old and new treatments applied on the same substrate.

The R&D groups in which this project falls ensure a multidisciplinary and scientific approach:

Analysis and Intervention in Architectural Heritage (AIPA), ETSAM-UPM.

Applied Petrology for Heritage Conservation (PAP), Geosciences Institute, CSIC-UCM.

3. Methodology

3.1 Bibliographical research

Exhaustive documentation about treatments, location, methodology of application, weather condition during treatment or, when possible, state of conservation before intervention, are crucial to evaluate aspects such as durability, efficacy and secondary effects [4]. These are in fact essential in order to distinguish causes of decay when observed in these areas, whether they are a direct reaction of the treatment itself or affected by external phenomena.

In the case of Mérida we have found detailed architectural projects from the sixties to the eighties for the reconstruction of most representative monuments of Roman Augusta Emerita, (Figure 2) and some modern reports regarding interventions from the nineties and early years of this century (Figure 3), which allow for a review of the evolution of criteria and methodology of interventions on archaeological remains.

First interventions are basically focused on anastilosis, or reconstruction works, of most monumental remains, like the theater, amphitheater or Temple of Diana. Mosaics and wall paintings, very numerous, have been traditionally extracted in block and transferred using new mounting systems with cement and an intern metallic armor, in some cases replaced from its original location. Negative consequences – listed below- are already visible (Figures 4-6).



Fig. 2: Resetting of the front stage in the Roman theater during the 20's (Source: LOTY archive, IPCE)

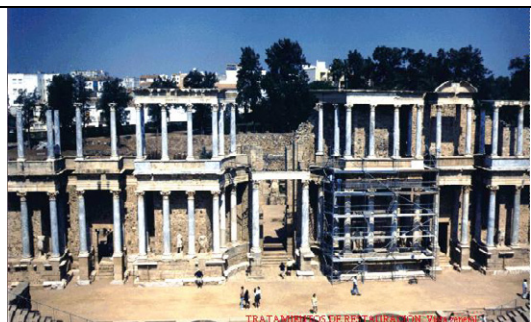


Fig. 3: Restoration works carried out in 1996 (Source: Agora S.L)

The methodology followed during the first projects is common in architectural or monumental restoration, changing by the early nineties, to see more standardized actions according to the development of criteria:

1/ Use of cement and reinforced concrete for structural consolidation, reconstruction and reintegration of elements.

2/ Synthetic resin (epoxy) for general consolidation of stone and as tie for reconstruction of fragments, as well as cement anchorages (Perfo[®] system, which involves the introduction of metallic capsules filled with epoxy resin and cement into the drills) and bronze or iron staples [11].

3/ Acrylic resins for consolidation of wall paintings and cement mortars for new supports (reinforced with metallic armor and metallic staples in some cases), cement applied during the past decade has been replaced by the use of natural lime mortar, similar to the original one, or prepared restoration mortars.

4/ Recent interventions: cleaning treatments (extensively use of chemical cleaning poultice AB57 [12]), organo-silicic compounds such as ethyl silicate for superficial consolidation treatment of stone and pavements, biocide treatments, lime mortars, with acrylic or epoxy resins, for structural consolidation, and water repellents for final protection.

Previous researches have focused on assessing and evaluating the effects of past treatments on stone material. First conclusions on the analysis of this reading are:

- Great advances have been achieved in terms of evaluation of stone treatments such as cleaning, consolidation and protection, largely focused in water repellents or hydrophobic products, but these have been mostly conducted on historic buildings and sculptures, rarely on archaeological sites, were particularities on material conservation after burial phase and excavation trauma require a different approach.

- Most of outcomes achieved from laboratory testing are mainly based on artificial ageing tests, but few of them have been carried out in the field.

- Research in stone conservation has a long tradition in identification of pathologies, mechanisms of degradation and development of treatments. The effects of some of these treatments in the mid and long-term, as well as detailed data about the degradation process are still poorly described.

- Retreatability is an open research field and still lacks deep research. Little work has been done on the effects that one treatment might have on another [13]. Concatenation of different treatments on the surface of archaeological remains and the lack of monitoring procedures, along with the fact that the remains are usually exposed to severe weathering conditions, lead to unpredictable damages that contribute to the general degradation of the site.

3.2 Field research

The main goal is to assess the conservation state of areas where interventions have been documented, trying to identify effects, alterations or indicators for further analysis.

The first observations allowed us to identify the following indicators of these effects (Figures 4-6):

- Problems arising from the use of synthetic resins: disadvantages of using these products on archaeological sites are related to the photodegradation process due to its exposure to weathering. This involves color changes, yellowing, and loss of mechanical properties caused by the action of solar radiation (ultraviolet irradiation), which involves chain scission, usually accompanied by the production of volatile compounds such as methanol, carbon dioxide, carbon monoxide, methyl formate, methane or hydrogen. This is particularly visible in the use of acrylic resins [14] when applied on superficial films, but also on epoxy resins used as an adhesive or fixing system. The fall of fragments of ornamental marble elements from the entablature of the front stage of the Roman Theater (most of them form the cornices and architraves) is one of the most serious problems associated with the latter, when the resin has been exposed to the environment losing its adhesive properties.

These kind of products are also extensively affected by biodegradation due to their organic nature. All polymers are potential substrates for the development of heterotrophic microorganisms, including bacteria and fungi [15]. Furthermore, in this depolymerization process, microorganisms emit organic acids, CO₂, CH₄ and H₂O, which if combined with other compounds can form harmful products.

- Decay arising from the use of cement or concrete due to different properties between the cement applied and traditional mortars. The major problem arising from the use of cement as a restorative material is the difference in its physico-chemical properties and those of traditional mortars present in the original fabric [16]. The greater resistance of cement makes it markedly more rigid than the material upon which it stands. This difference in elasticity creates an area of big tension between both materials. The thermal expansion between stone or brick and cement can be twice higher, which results in strong internal tensions that lead to fissures and cracks (Figure 4), allowing the access of moisture and thus biodegradation.

Physical damages are caused by the cements low permeability to water vapor, used as mounting system for the mosaics, and dampness from soil. The replacement of cemented pavement prevents transpiration and thus movement of



Fig. 4: Granitic column with reintegration of cement in the House of Mitreo

water to lateral walls. Water absorption by capillarity has seriously damaged wall paintings and has motivated a new intervention in order to “restore former restoration”, by removing cement reintegration of the mosaic and temporally filling the voids with gravel (Figure 5).

In addition to the physical and mechanical damages, the unstable chemical composition of cement leads to problems due to the formation of salts that migrate into the pore system of the archaeological stone material. It is particularly sensitive to sulfur compounds, so that in polluted environments and in the presence of sulfate is rapidly degraded.

- Mechanical damages from the use of metal elements: bursting due to corrosion and expansion of a metal fixing and rust stains (Figure 6).



Fig. 5: Degradation around the skirting board of the wall paintings in the Tablinum of Basilica's House, inside the Theater area.



Fig. 6: Wall paintings deteriorated by the metallic armor in the peristyle of House of Mitreo.

3.3 Analytical testing

After identifying treated and untreated areas in selected archaeological sites the aim is the comparison of the state of conservation of both materials, and to assess the effectiveness, durability or deteriorating effects of conservation/restoration products documented.

Results from first measurements, carried out recently on the site of House of Mitreo (Figures 7 and 8), show interesting figures. We are still working on the interpretation and analysis of these results, however, it can be mentioned some interesting data from direct measurements of the propagation velocity of ultrasound (V_p , Pundit equipment), the most remarkable one is shown by the different values in US velocity between treated (with acrylic resin) and untreated areas. The values recorded by indirect method shows that propagation velocity is higher in the treated area (between 2000 and 2500 m/s) compared to the untreated area (ranging from 1580 to 1765 m/s); this means that the cohesive consolidation appears to have been effective, given that voids have been filled (fostering the propagation of US). Structural disintegration of the stone causes the reduction of velocity of propagation of US. This provides information on the state of the conservation of material, allowing for the recognition of altered or weak areas or elements with different quality of preservation. The pulse propagation time is directly related to the materials density, and the presence of voids, any hole, crack or fracture, slows down the velocity of the waves. It is especially useful to evaluate consolidating treatments, making comparative tests

between the material before and after treatment, checking if its application provides greater cohesion or produces changes in the pore system.



Fig. 7: US measurements on treated area of wall painting in Room 13, House of Mitreo.



Fig. 8: Measurements with portable Raman, Atrium of the House of Mitreo.

Some changes in the superficial texture of some wall paintings can be observed by using optical surface roughnessmeter (TRACEiT, Innwep GmbH). It allows 3D roughness topographic maps and obtains values for Ra, Rq and Rz roughness parameters according to DIN EN ISO4287 standard. This factor influences the degree of degradation in relation to the specific surface of the material; a rougher surface could help soiling and water retention, and accelerate material decay due to a specific surface increase (more reactive) [17]. At first sight it seems that superficial texture is more homogeneous in untreated areas (Rq factor has a value of 2,50 along the x axis, and 2,62 along the y axis) and more rough in treated ones, with acrylic resin (Rq factor has a value of 2,74 along the x axis, and 3,01 along the y axis). Rq factor shows the increase of rough in the second case. Nevertheless, it is necessary a deeper knowledge about all variables present to determine the influence of the treatment in the roughness increase, the fragments of wall painting analysed from the cistern (Room 17) of House of Mitreo are part of the collection of the National Museum of Roman Art of Merida. It can also be observed changes in the roughness of the different pigments (Figure 9), taking into account that comparable studies must be analysed by colours (the Rq values mentioned are from light red pigment).

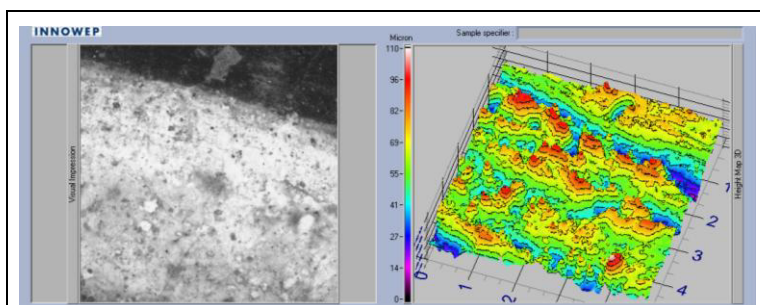


Fig. 9: White and blue pigments are clearly distinguishable by the bond line and a different roughness

For this same purpose we can count with other several techniques of characterization:

- Identification and characterization of former treatments:

By the use of portable and non-destructive techniques such as Raman, μXRF or μFTIR, which allow us to analyze organic and inorganic compounds.

SEM-EDS (Scanning electron microscopy) combines observation of images at micro and nanometric scale and elemental analysis of the material composition. It is very useful in the comparative study of treated and untreated areas, comparing composition, texture or porosity, and for the observation of depth of penetration of treatment in the substrate.

Petrographic analysis with Polarizing Optical Microscopy (POM): size, composition and bonding crystals/grains of the material, porous material system, mineralogy, etc.

Magnetometry for the detection of metallic elements in the interior of structures. Some metallic elements, previously unknown, have been detected underneath the Cosmologic Mosaic.

- Determination of the effects of treatments in original stone material:

The Spectrophotometric color measurement is used in stone conservation to assess the effects of some treatments such as cleaning or consolidation, as well as monitoring the re-soiling of the surface after the proceedings [18]. This method is not only important to determine changes for aesthetic reasons but it can also help understand mechanisms of alteration of the material when exposed to weathering. These changes can be due to chemical processes of dissolution, alteration of mineral compounds or by the formation of aging patina on the material surface.

- Determination of the effectiveness of consolidant treatments:

Drilling Resistance Measuring System (DRMS): measures the resistance of stone material to perforation. The response of the material provides information about aspects such as compactness and hardness, which in the field of conservation of cultural heritage translates into a greater awareness of the conservation status of the material, mainly the thickness of altered layer, or of the consolidated depth, and thereby establishes better guarantees for the necessary maintenance procedures.

Depth of penetration by Nuclear Magnetic Resonance (NMR) to study the water transport behavior inside the stone material.

Transformation of the porous system with Mercury Intrusion Porosimetry: it is an indirect and destructive technique for the characterization of porous system, which allows us to know the total pore volume, the pores size and distribution (macro and microporosity) and tortuousness of the porous system, factors all of them determinants for conservation and durability of stone material.

Finally, Infrared Thermography (IT) to determine changes in thermal behavior of materials or the existence of decayed areas.

4. Conclusions

Historical reviews are critical in order to have real data on the state of archeological heritage sites, considering, in several cases, certain conservation techniques and restoration treatments as an agent of deterioration, within the group of human factors. It is also relevant in order to assess a comprehensive diagnosis and determination of pathologies. Researching the durability and efficiency of restoration treatments is crucial for the application of realistic and long-term conservation measures.

In situ measurements and the characterization of treated and untreated stone material is a simple procedure to assess the state of ancient interventions, however it is not often included in standardized conservation of archaeological sites.

The results of this study will foster the development of a standard operating protocol, providing a scientific basis for future intervention methodologies, as examples described in other disciplines as international and European rules.

Finally, increased knowledge on the effects of past interventions is critical for improved management of present and future intervention projects, particularly when such areas have become a source of degradation.

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